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Metal-Complexing Ligands and Metal Speciation in Sediment Pore Waters: Implications for Sediment/Water Exchange and Water Column Speciation

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13. ABSTRACT (Maximum 200 words)

Fluxes of TDCu and Cu ligands have been determined at two sites in the Chesapeake Bay for June and October '95, and in March '96. TDCu appears to flux out of the sediments at both sites in both spring and summer. In March '95, the TDCu flux out of site M (mid-Bay) sediments (41 ± 10 nmol/m²/d) exceeded that at site S (southern Bay: 7 ± 3 nmol/m²/d). However, in June '95, the TDCu flux out at site S (52 ± 25 nmol/m²/d) exceeded that at site M (13 ± 15 nmol/m²/d). There is a significant out-flux (200 to 800 nmol/m²/d) of total Cu-binding ligands (TL_{Cu}) from the sediments at both sites in both spring and summer, but the TL_{Cu} flux at site M exceeded that at site S. The TL_{Cu} is 3-60x greater than the TDCu flux, and the ligands fluxing out are comparable in strength ($\log K' = 15$) to that of the very strong L₁ class that controls the speciation of TDCu in most marine surface waters, and previously only observed in these surface waters. Sediment fluxes of this very strong ligand in June '95 ranged from 200 to 600 nmol/m²/d, representing up to 50% of the sediment TL_{Cu} flux, and exceeded the TDCu by up to 20x. Thus, sediments may be a significant, but previously-unrecognized, source of Cu-complexing ligands to overlying waters.

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METAL-COMPLEXING LIGANDS & METAL SPECIATION IN SEDIMENT PORE WATERS: IMPLICATIONS FOR SEDIMENT/WATER EXCHANGE & WATER COLUMN SPECIATION (ONR GRANT N00014-93-1-0899)

LONG-TERM GOALS

Our long-term goals are to determine the role that complexation and speciation play in sediment/water exchange of metals in estuarine and coastal locations; and the importance of metal-complexing ligands fluxing out of estuarine pore waters to metal speciation on local, regional, and global scales.

SCIENTIFIC OBJECTIVES

Our scientific objectives are to determine: (1) the extent of complexation and the speciation of selected trace metals in bottom waters and sediment pore waters; (2) concentrations and strengths of metal ligands in bottom waters and sediment pore waters; (3) the magnitude and direction of the benthic flux of metals and their ligands; and (4) the lifetime of the metal ligands fluxing out of pore waters into overlying bottom waters and their degradation processes.

APPROACH.

Our approach consists of both field and laboratory efforts. We sampled the sediments and water column from two estuarine sites (M and S) in Chesapeake Bay having contrasting biogeochemical and physical characteristics during spring, summer, and fall. Cores were also collected in the heavily anthropogenically-impacted Elizabeth River in March '96, and at a site along the mid-Atlantic shelf/slope break (WC7) in June '95 and August '96.

Sediments were collected using a stainless steel box corer, and subsampled using acid-cleaned plexiglass core tubes, and clean shoulder-length polyethylene gloves. All pore water samples were obtained from sediment cores sectioned under N₂ and centrifuged at *in situ* temperatures. Surface and bottom water samples were collected with either a peristaltic pumping system through Teflon tubing attached to a weighted plastic "fish-vane", or with a 30-liter GO-Flo bottle. Concentrations of total dissolved Cu (TDCu: 0.45 or 0.22 μ m-filtered) were determined by chemiluminescence;

total dissolved Zn (TDZn) concentrations were determined by differential pulse anodic stripping voltammetry (DPASV). Cu and Zn complexation and speciation were determined by ASV (differential pulse or square wave modulation) at a rotating thin mercury film/ glassy carbon disk electrode, hanging mercury drop electrode, and by ligand competition/ adsorptive cathodic stripping voltammetry. Pore water concentrations of dissolved organic carbon were determined by high temperature catalytic oxidation, while pore water Fe, Mn, sulfide, nutrients, and $\sum \text{CO}_2$ were determined by standard methods.

TASKS COMPLETED

Fluxes of TDCu and Cu ligands have been determined using incubated sediment cores and bottom waters collected on cruises in June and October '95, and in March '96. Spatial and temporal studies of TDZn, TDCu, TDCd concentrations, complexation, and speciation in the Chesapeake Bay water column have been completed.

Work in progress includes data workup and/or determination of the concentrations of TDCu and TDZn, Cu and Zn ligands, sulfide, DOC, Fe, Mn, nutrients and $\sum \text{CO}_2$ in sediment pore waters, and concentrations of TDCu and TDZn, Cu and Zn ligands, and sulfide in bottom and surface waters, in samples collected on cruises in March, August and October, '96. In addition, we are presently conducting an experiment to study the degradation rates of Cu ligands isolated from sediment pore waters at site M in October '96.

We've presented our results at national meetings and have submitted or are preparing manuscripts on: (1) the speciation of TDCu in the pore waters and bottom waters of Chesapeake Bay (Skrabal, Donat, and Burdige, in prep.; 1995 American Chemical Society meeting; 1995 Gordon Research Conference); (2) the flux of Cu ligands from estuarine sediments (Skrabal, Donat, and Burdige, in review; 1996 Ocean Sciences meeting; abstract submitted for 1997 ACS meeting); (3) Zn complexation and speciation in the Chesapeake Bay water column (Henry and Donat, in prep; 1996 Ocean Sciences meeting; abstract submitted for 1997 ACS meeting); and (4) Cu and Cd speciation in the Chesapeake Bay water column (Donat, two manuscripts in prep; 1995 American Chemical Society meeting; 1995 Gordon Research Conference).

RESULTS

TDCu concentrations in the pore waters from sites M, S, and WC7 range from 0.1 to 25 nM, and were usually ≤ 10 nM. These concentrations were generally similar to bottom water concentrations, and are quite low compared to other anthropogenically-impacted estuaries (e.g., Narragansett and San Francisco Bays). TDCu appears to flux out of the sediments at both sites M and S in both spring and summer. In March '95, the TDCu flux out of site M sediments (41 ± 10

nmol/m²/d) exceeded that at site S (7±3 nmol/m²/d). However, in June '95, the TDCu flux out at site S (52±25 nmol/m²/d) exceeded that at site M (13±15 nmol/m²/d).

Our results indicate a significant out-flux (200 to 800 nmol/m²/d) of total Cu-binding ligands (TL_{Cu}) from the sediments at both sites in both spring and summer, but the TL_{Cu} flux at site M exceeded that at site S. The TL_{Cu} is 3-60x greater than the TDCu flux, and the ligands fluxing out are comparable in strength (log K'=15) to that of the very strong L₁ class that controls the speciation of TDCu in most marine surface waters, and previously only observed in these surface waters. Sediment fluxes of this very strong ligand in June '95 ranged from 200 to 600 nmol/m²/d, representing up to 50% of the sediment TL_{Cu} flux, and exceeded the TDCu by up to 20x. Thus, sediments may be a significant, but previously-unrecognized, source of Cu-complexing ligands to overlying waters. We are examining TDCu and TL_{Cu} fluxes with respect to solid phase metal concentrations and speciation in these sediments, obtained as a part of our collaborative effort with Prof. John Morse at Texas A & M. We collected these sediment cores for Morse's group during our field studies, and we are currently working with Prof. Morse on the interpretation of this data.

TDZn concentrations in Chesapeake Bay ranged from 3 to 40 nM. From 84% to ≥99% of TDZn is organically-complexed with a single strong ligand class (log K'_{ZnL, Zn'} = 9-10), whose concentration ranges from 2 to 10x that of TDZn. Ligand concentrations were greatest in the north Bay and decreased by 10x toward the Bay mouth. Zn²⁺ concentrations ranged from about 20 to 300pM, which are between levels reported to be limiting and toxic to marine phytoplankton.

Impacts for Science

The speciation of metals in sediment pore waters governs both the fate of metals (by controlling the extent and speed of their cycling between sediments and the water column), and their effects on biota (by influencing bioaccumulation and toxicity). Our results indicate that pore waters contain very strong Cu ligands in very high concentrations, which should markedly influence the sediment/water exchange of Cu. These very strong ligands are fluxing out into the water column, where they may influence the fate and effects of Cu in estuarine and coastal water columns.

Relationships to Other Projects

Our results compliment other ONR projects on organic diagenesis and metal cycling in sediments (Berelson, Johnson and Coale), metal speciation in sediment solid phases (Morse), physico-chemical speciation of bioactive metals in the water column (Bruland), and metal-phytoplankton interactions (Moffett and Brand, Sunda).

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METAL COMPLEXING LIGANDS & METAL SPECIATION IN SEDIMENT PORE
WATERS: IMPLICATIONS FOR SEDIMENT/WATER EXCHANGE & WATER
COLUMN SPECIATION (ONR GRANT N00014-93-1-0899)

PUBLICATIONS

Book Chapters

Donat, J.R. and K.W. Bruland. 1995. Trace Elements in the
Oceans, Chapter 11 in: Trace Elements in Natural Waters,
B. Salbu and E. Steinnes, Eds. 302 p.

Refereed Papers

Skrabal, S.A., J.R. Donat, and D.J. Burdige. Fluxes of
Copper-Complexing Ligands from Estuarine Sediments.
Manuscript in review, Limnology and Oceanography.

Skrabal, S.A., J.R. Donat, and D.J. Burdige. Copper
complexation in estuarine and coastal sediment pore waters:
Implications for Sediment/Water Exchange. Manuscript in
preparation.

Invited Conference Presentations

Donat, J.R., S.A. Skrabal, and D.J. Burdige. 1995. "Copper
complexation in pore waters and bottom waters of Chesapeake
Bay and the Atlantic shelf/slope". 209th National Meeting of
the American Chemical Society, Anaheim CA.

Donat, J.R. 1995. "The speciation of copper and cadmium in
the Chesapeake Bay". 209th National Meeting of the American
Chemical Society, Anaheim CA.

Donat, J.R., S.A. Skrabal, and D.J. Burdige. 1996. "Effect
of Speciation on sediment-Water Exchange of Metals".
Presented at ONR's Harbor Processes Program Workshop,
Arlington, VA.

Contributed Conference Presentations

Skrabal, S.A., J.R. Donat, and D.J. Burdige. "Fluxes of
strong copper-complexing ligands from estuarine sediments: A
source to the water column?". Abstract submitted to the ACS
National Meeting, San Francisco, April 1997.

Donat, J.R. and C.W. Henry, III. "Concentrations, complexation, and speciation of dissolved zinc in Chesapeake Bay". Abstract submitted to the ACS National Meeting, San Francisco, April 1997.

Zheng, S. and D.J. Burdige. "Dissolved organic nitrogen fluxes in coastal and estuarine sediment pore waters". Abstract submitted to the ASLO '97 Meeting, Santa Fe, February 1997.

Skrabal, S.A., J.R. Donat, and D.J. Burdige. 1996. "The flux of copper-complexing ligands from Chesapeake Bay sediments". Ocean Sciences Meeting, San Diego, CA.

Henry, C.W. III and J.R. Donat. 1996. "Zinc complexation and speciation in the Chesapeake Bay". Ocean Sciences Meeting, San Diego, CA.

Burdige, D.J., K.G. Gardner, and S. Zheng. 1996. "The molecular weight distribution of dissolved organic matter (DOM) in marine sediment pore waters". Ocean Sciences Meeting, San Diego, CA.

Zheng, S. and D.J. Burdige. 1996. "The geochemistry of dissolved organic nitrogen in coastal sediment pore waters". Ocean Sciences Meeting, San Diego, CA.

S.A. Skrabal, J.R. Donat, and D.J. Burdige. 1995. "The speciation of copper in pore waters and bottom waters of Chesapeake Bay and Atlantic coastal waters: Implications for sediment-water exchange". Gordon Conference on Chemical Oceanography, Henniker, NH.

Number of undergraduate students supported

3

Number of graduate students supported

3

Number of post-docs supported

2

Number of other technical personnel supported

1

Number of Asian graduate students supported

1

Honors/Awards

J.R. Donat. Undergraduate Chemistry/Biochemistry Teacher of the Year, 1995. Dept. of Chemistry/Biochemistry, Old Dominion University.